



04/25/97

## W. G. FASSE

PATENT ATTORNEYS

INDIAN POND LANE (P.O. Box K)  
ST. ALBANS, MAINE 04971-0133TELEPHONE: 207-938-4422  
TELEFAX: 207-938-2323

April 25, 1997

WOLFGANG G. FASSE

WALTER F. FASSE

BY EXPRESS MAIL SERVICE:  
CERT. NO.: EM407058465US60854 U.S. PTO  
00843124ASSISTANT COMMISSIONER FOR PATENTS  
BOX NEW PAT APP  
WASHINGTON, D. C. 20231

Re: NEW PATENT APPLICATION  
 Attorney Docket No.: 3442  
 Inventor: 1) Tomohiro Kawase 2) Masami Tatsumi  
 Title: METHOD OF PREPARING GROUP III-V COMPOUND  
 SEMICONDUCTOR CRYSTAL

Dear Sir:

1) I am enclosing a NEW PATENT APPLICATION comprising:  
 a) 26 pages of specification; 20 claims; ( 1 independent);  
8 Figs. on 7 sheets of drawings;  
 an abstract;  
1 return receipt postcard;  
 Express Mail Certificate;  
 b) Declaration, Power of Attorney;  
 c) My check #7709 in the amount of \$770.00 to cover the filing  
 fee. Any deficiency should be charged to Deposit Account No.:  
 06-0240;  
 d) an assignment and Recordation Form Cover Sheet;  
 e) an Information Disclosure Statement, form PTO-1449, 5 references.

## 2) The Priority of earlier application:

Country: Japan

Application No.: 8-107009 Filed: April 26, 1996

is hereby expressly claimed under 35 U.S.C. 119.

## 3) The Priority Document will follow.

Very truly yours,

W. G. Fasse  
 Patent Attorney  
 Reg. No.: 21187

WGF:me/3442

Encls.: as listed above

BY EXPRESS MAIL SERVICE:  
CERT. NO.: EM407058465US  
=====  
Docket No.: 3442

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
IN THE MATTER OF THE NEW APPLICATION FOR PATENT  
of: Tomohiro Kawase et al.

Serial No.: TO BE ASSIGNED

Filed: April 25, 1997

Title: METHOD OF PREPARING GROUP III-V COMPOUND SEMICONDUCTOR  
CRYSTAL

ASSISTANT COMMISSIONER FOR PATENTS  
BOX PATENT APPLICATION  
WASHINGTON, D. C. 20231

TYPE OF PAPER BEING DEPOSITED: A NEW PATENT APPLICATION,  
comprising 26 pages of specification, 20 claims on 5 pages, an  
abstract, a Declaration, 8 Figs. on 7 sheets of drawings;  
ck#7709 in the amount of \$770.00 to cover the filing fee; a Cover  
Letter to the Commissioner, a return receipt postcard, an assignment  
and Recordation Form Cover Sheet, IDS, form PTO-1449, 5 references.

CERTIFICATE OF EXPRESS MAIL SERVICE

NUMBER: EM407058465US

DATE OF DEPOSIT: April 25, 1997

I hereby certify that I am depositing this correspondence with  
the United States Postal Service "EXPRESS MAIL POST OFFICE TO  
ADDRESSEE" service under 37 CFR 1.10 on the date indicated above,  
addressed to: ASSISTANT COMMISSIONER FOR PATENTS, BOX NEW PAT  
APP, Washington, D. C. 20231.

Margit Ettlinger Apr. 25.97  
ANIKESMORSE - April 25, 1997  
Margit Ettlinger

TITLE OF THE INVENTION

Method of Preparing Group III-V Compound Semiconductor  
Crystal

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a method of preparing a group III-V compound semiconductor crystal. Particularly, the present invention relates to a method of preparing a group III-V compound semiconductor crystal in 10 which carbon is doped.

Description of the Background Art

Conventionally, there are various prior arts as set forth in the following regarding the method of preparing a group III-V compound semiconductor crystal in which carbon 15 is doped.

In Japanese Patent Laying-Open No. 64-79087 (referred to as "prior art 1" hereinafter), a method of preparing a carbon-doped GaAs single crystal according to the gradient freeze method or horizontal Bridgman method (HB method) is 20 disclosed.

Fig. 6 is a diagram for describing a method of preparing a carbon-doped GaAs single crystal according to prior art 1.

Referring to Fig. 6, a graphite boat 51 as a carbon 25 source is arranged at one side in a quartz ampoule 55. Raw

material which is gallium (Ga) 52 is provided in graphite boat 51. Arsenic (As) 57 is provided at the other side in quartz ampoule 55. Quartz ampoule 55 is sealed in vacuum and then installed in an electric furnace to be heated.

5 After the GaAs raw material is synthesized, the temperature is reduced maintaining a constant temperature gradient, whereby a GaAs single crystal is grown.

10 The carbon of graphite boat 51 reacts with oxygen supplied from  $As_2O_3$ ,  $Ga_2O$  and the like remaining in quartz ampoule 55 to result in gas of  $CO$ ,  $CO_2$  and the like to be doped into the growing GaAs crystal.

15 It is described that the doping amount of carbon can be controlled according to the total amount of oxygen in the sealed quartz ampoule 55, the synthesization reaction condition, or single crystal growth condition, and the like.

20 In Journal of the Japanese Association of Crystal Growth, 1991, Vol. 18, No. 4, pp. 88-95 (referred to as "prior art 2" hereinafter), a method of preparing a carbon-doped GaAs single crystal by the vertical gradient freeze method (VGF method) is disclosed.

Fig. 7 is a diagram for describing a method of preparing a carbon-doped GaAs single crystal according to prior art 2.

25 Referring to Fig. 7, raw material 62 having carbon

doped in advance, directly synthesized by the LEC method and boron oxide (B<sub>2</sub>O<sub>3</sub>) 64 are provided in a crucible 61 and sealed in vacuum in a quartz ampoule 65. This is installed in a vertical furnace and heated to melt the raw material and boron oxide. By reducing the temperature in the furnace while maintaining a constant temperature gradient, a GaAs single crystal is grown.

5       Here, boron oxide containing water of 200ppm spreads around only the periphery of the upper surface of GaAs melt 62. The center area of the upper surface of GaAs melt 10 62 is exposed to the ambient. According to the method of prior art 2, the upper surface of the melt must be exposed to the ambient to control the stoichiometry of the GaAs melt. The vapor pressure in quartz ampoule 65 is 15 controlled by arsenic 67.

According to this method, the carbon concentration of the crystal depends on the carbon concentration of the raw material.

In U.S. Patent No. 4,999,082 (referred to as "prior 20 art 3" hereinafter), a method of preparing carbon-doped GaAs single crystal by the vertical Bridgman method (VB method) is disclosed.

25       Fig. 8 is a diagram for describing a method of preparing carbon-doped GaAs single crystal according to prior art 3.

Referring to Fig. 8, a crucible 71 is filled with GaAs raw material 72. After carbon source 73 is arranged outside of crucible 71, a quartz ampoule 75 is sealed. Quartz ampoule 75 is placed in a vertical furnace and 5 heated to melt the raw material. The furnace is moved upwards while substantially maintaining the set temperature profile. By solidifying the raw material from a seed crystal 77, a GaAs single crystal is grown.

According to this method, carbon source 73 is in 10 fluid communication with compound raw material 72 to allow gas transfer.

Japanese Patent Laying-Open No. 3-252399 (referred to as "prior art 4" hereinafter) discloses a method of preparing a semi-insulating GaAs substrate.

15 Prior art 4 is characterized in that the impurity which becomes the acceptor is doped so as to result in  $1\sim 3 \times 10^{15}$  atoms/cm<sup>3</sup> after subtracting the concentration of the impurity which becomes the donor in a GaAs crystal.

Japanese Patent Laying-Open No. 2-74597 (referred to 20 as "prior art 5" hereinafter) discloses a chromium-doped semi-insulating GaAs single crystal and a method of preparing thereof. This prior art 5 is characterized in that carbon is contained having a concentration  $n_c$  that satisfies both the relations of:

25  $1 \times 10^{15} \text{ cm}^{-3} \leq n_c < n_{si}$  and  $n_{si} - n_c \leq 4.4 \times 10^{15} \text{ cm}^{-3}$

for the residual Si concentration of  $n_{Si}$  remaining in the single crystal, with the resistivity of at least  $10^6 \Omega \cdot cm$ .

The above-described prior art have various disadvantages. In prior art 1, boron oxide is not used. 5 Therefore, impurity contamination can be expected. Furthermore, since the amount of the carbon source cannot be controlled in this method, it is difficult to control the carbon concentration.

In prior art 2, carbon cannot be doped during the 10 crystal growth since carbon source is not used. There is a problem that the carbon concentration cannot be adjusted during crystal preparation. Furthermore, a part of the carbon in the GaAs melt reacts with oxygen, that is generated as a result of the water in the boron oxide 15 decomposing, to be lost as CO gas. There was a problem that the carbon concentration in the GaAs crystal is lowered.

In prior art 3, it is difficult to control the carbon 20 concentration since the carbon source is located outside the crucible. Furthermore, impurity contamination can be expected since boron oxide is not used.

In prior art 4, carbon is recited as the impurity 25 serving as the acceptor. However, only the doping of zinc and copper is disclosed as the example. There is no description of carbon doping.

Prior art 5 describes a chromium-doped semi-insulating GaAs single crystal containing carbon. However, this prior art 5 is silent about the method of doping carbon.

## 5 SUMMARY OF THE INVENTION

In view of the foregoing, an object of the present invention is to provide a method of preparing in high reproducibility a group III-V compound semiconductor crystal of favorable electrical characteristics having impurities removed, and in which the amount of doped carbon can easily be adjusted during crystal growth.

According to an aspect of the present invention, a method of preparing a group III-V compound semiconductor crystal is provided. This method of preparing a group III-V compound semiconductor crystal having carbon doped includes the steps of: filling a crucible or boat with compound raw material, solid carbon, and boron oxide; sealing the crucible or boat filled with compound raw material, solid carbon, and boron oxide in an airtight vessel formed of a gas impermeable material; heating and melting the compound material in a sealed state in the airtight vessel; and solidifying the melted compound material to grow a carbon-doped compound semiconductor crystal.

25 Since the crucible or boat is filled with compound

raw material, solid carbon, and boron oxide according to the present invention, the boron oxide softened by heating is brought into contact with at least a portion of the solid carbon in the state where the compound raw material 5 is melted.

According to the present invention, the carbon concentration in the raw material does not have to be adjusted since carbon can be doped during crystal growth. Good controllability of the carbon concentration is 10 obtained. In other words, the target carbon concentration can be obtained in high reproducibility. By using boron oxide which has an impurity removal effect, the contamination of impurities in the crystal can be suppressed to obtain a crystal of favorable electrical 15 characteristics.

Quartz or pBN (pyrolytic boron nitride) and the like can be enumerated as the gas impermeable material.

Preferably, boron oxide contains water.

This is because the water in boron oxide is essential 20 to remove impurities. Furthermore, it is considered that the water in the boron oxide effects the incorporation of carbon into the crystal.

Boron oxide preferably contains water of 10-500 wt ppm.

25 In the present invention, the amount of solid carbon

to be filled is preferably larger than the amount of carbon doped into the compound semiconductor crystal.

This is to promote reaction using an excessive amount of carbon since the reaction rate of solid carbon is extremely low. Furthermore, consumption of the part of the solid carbon at the gas generation of the carbon compound must be supplied. Thus, by using solid carbon of an amount larger than the total amount of carbon doped into the crystal, the advantage of the present invention works effectively.

Specifically, the amount of solid carbon must be at least ten times, preferably at least 100 times larger than the weight of the carbon doped into the crystal.

In the present invention, it is preferred that the solid carbon is subjected to a heat treatment under reduced pressure before being filled in the crucible or boat.

By this process, the impurity element remaining in carbon is removed to result in a crystal of higher purity.

The pressure in applying a heat treatment on carbon is preferably from 1 Torr to  $1 \times 10^{-8}$  Torr. The appropriate temperature of the heat treatment is 500°C-2000°C. The above-described effect can be obtained by carrying out the heat treatment for at least one hour. It was found that a greater effect can be obtained as the time for the heat

treatment becomes longer. However, there is very little change in the effect when the time for the heat treatment exceeds 12 hours. Considering that the cost for production is increased as the time for the heat treatment becomes 5 longer, the time period for the heat treatment of not more than 12 hours is appropriate.

In the present invention, it is preferable to keep the compound raw material in its melted state for a certain time period before it is solidified for crystal 10 growth.

By this process, the impurities of Si and the like in the GaAs polycrystalline raw material can be removed by gettering with boron oxide. Although Si of approximately  $1 \times 10^{16} \text{cm}^{-3}$  is included as impurities in the raw material 15 synthesized by the HB method, the amount of Si in the GaAs subjected to the above-described process is less than  $1 \times 10^{15} \text{cm}^{-3}$ , which is below the detection limit of an analyzer. Si of an amount over  $1 \times 10^{15} \text{cm}^{-3}$  was detected from those not subjected to the above-described process.

20 Thus, carbon can be sufficiently melted in the GaAs melt from the solid carbon by the above-described process. This process also provides the advantage that the temperature of the GaAs melt is stabilized, and the carbon concentration and impurity concentration in the melt can 25 be made uniform.

The above-described effect can be obtained when the holding time period in the melted state of raw material is at least 3 hours. Further favorable characteristics can be obtained stably when the holding time is at least 6 hours.

5 Although a greater effect can be obtained as the holding time becomes longer, the degree of change in the effect gradually becomes smaller when the holding time period exceeds 36 hours. There is very little change in the effect when the holding time exceeds 72 hours. Considering 10 that the cost for production becomes higher as the holding time is increased, the holding time is preferably not more than 72 hours, further preferably not more than 36 hours.

In the present invention, powder carbon can be used as the solid carbon.

15 Powder carbon is advantageous in promoting the reaction due to its greater specific surface area. Increase in the reaction speed allows carbon to be doped efficiently in the crystal.

Also, the amount of carbon to be doped into the 20 crystal can easily be adjusted according to the grain size, the weight, and the like of the used powder. For example, powder of a smaller grain size has a greater specific surface area to increase the reaction speed, whereby the amount of doped carbon is increased.

25 Therefore, the grain size of the powder carbon is

preferably smaller. More specifically, the average grain size is preferably not more than 100 $\mu\text{m}$ , more preferably not more than 50 $\mu\text{m}$ . When powder carbon is used, the powder carbon spreads in the boron oxide softened by heating in the state where the compound raw material is melted.

5 In the present invention, fiber carbon, as well as powder carbon, can be used as the solid carbon.

Fiber carbon is advantageous in that the diameter of the fiber is small and a greater surface area can be obtained to result in a faster reaction speed. It is therefore possible to dope carbon into the crystal efficiently. Also, the amount of carbon doped into the crystal can easily be adjusted according to the diameter or weight of the fiber that is used. Uniform distribution 10 of the carbon concentration can be obtained from the shoulder to the tail of the prepared crystal when fiber 15 carbon is used.

The diameter of the fiber carbon is preferably smaller. Specifically, the average diameter is preferably not more than 50 $\mu\text{m}$ , more preferably not more than 10 $\mu\text{m}$ .

Usage of fiber carbon allows carbon to spread in boron oxide that is softened by heating in the state where the compound raw material is melted. Also, the carbon can float above boron oxide to be exposed to the ambient.

25 In the present invention, bulk carbon can be used as

solid carbon, in addition to powder carbon and fiber carbon.

Bulk carbon is advantageous in that the amount of carbon to be doped in the crystal can easily be adjusted 5 by the weight and configuration of the carbon used.

Uniform distribution of carbon concentration can be obtained from the shoulder to the tail of the prepared crystal when bulk carbon is used.

Bulk carbon is preferably used in a disk shape that 10 is smaller than the inner diameter of the crucible. The amount of doped carbon can easily be controlled by the diameter of the disk.

The bulk solid carbon is preferably a sintered compact of carbon powder. The reaction speed is 15 particularly high for the sintered compact of powder having high porosity. Sintered carbon powder is advantageous in distributing carbon uniformly in the crystal.

When bulk solid carbon is used, a state can be 20 obtained in which at least a portion of the bulk solid carbon is immersed in the softened boron oxide.

In the present invention, the crucible or boat is preferably formed of pBN (pyrolytic boron nitride).

Depending upon the constituent element of the 25 crucible or boat, there is a possibility that boron oxide

or carbon reacts with the crucible to induce contamination of the raw material melt. pBN is most appropriate as the material of the crucible or boat to suppress reaction with boron oxide or carbon.

5        The present invention is particularly effective as a method of doping carbon into a GaAs crystal.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the 10 present invention when taken in conjunction with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram for describing an example of a method of preparing a group III-V compound semiconductor 15 crystal according to the present invention.

Fig. 2 is a diagram showing the state of carrying out crystal growth using a vertical furnace.

Fig. 3 is a diagram for describing another example of a method of preparing a group III-V compound semiconductor 20 crystal according to the present invention.

Fig. 4 is a diagram for describing a further example of a method of preparing a group III-V compound semiconductor crystal according to the present invention.

Fig. 5 is a diagram for describing each portion of a 25 crystal.

Fig. 6 is a diagram for describing a method of preparing a carbon-doped group III-V compound semiconductor crystal single crystal according to an example of prior art.

5 Fig. 7 is a diagram for describing a method of preparing a carbon-doped group III-V compound semiconductor crystal single crystal according to another example of prior art.

10 Fig. 8 is a diagram for describing a method of preparing a carbon-doped group III-V compound semiconductor crystal single crystal according to a further example of prior art.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### Example 1

15 Fig. 1 is a diagram for describing an example of preparing a group III-V compound semiconductor crystal according to the present invention.

Referring to Fig. 1, GaAs polycrystalline raw material 2, carbon powder 13 subjected to heat treatment 20 under reduced pressure in advance, boron oxide ( $B_2O_3$ ) 4, and a seed crystal 7 were placed in a pBN crucible 1. The seed crystal was placed at the bottom portion of the crucible 1. In crucible 1, arrangement was provided so that carbon powder 13 and boron oxide 4 were brought into 25 contact with each other, and also boron oxide 4 and raw

material 2 were brought into contact with each other when the raw material was melted.

Crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Ampoule 5 was sealed under 5 reduced pressure with a quartz cap 6.

Respective conditions of Example 1 are shown in the following Table 1.

Table 1

GaAs polycrystal (raw material)	3kg used
Carbon powder	350 mesh (grain size 45 $\mu$ m and below), 100mg used Heat treatment at 1000°C for 6 hours at the pressure of 10 <sup>-2</sup> Torr
B <sub>2</sub> O <sub>3</sub>	Water concentration 50 wt ppm, 50g used
pBN crucible	Inner diameter 80mm, entire length 250mm
Solid arsenic	1g used

10

Referring to Fig. 2, the above-described quartz ampoule 5 was heated at the rate of approximately 200°C/hour by a heater 8 using a vertical furnace 50.

During this process of heating, boron oxide 4 was 15 softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a

film 4a having a thickness of less than 1mm between pBN crucible 1 and GaAs raw material melt 2. The remainder of boron oxide 4 covered the upper surface of GaAs melt 2. The thickness of the boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 5mm. Carbon powder 13 was dispersed in this boron oxide layer 4b.

5 The condition mentioned above was kept for approximately 36 hours.

Then, heater 8 was moved upwards at the rate of 10 4mm/hour, whereby solidification started from the portion of seed crystal 7. Thus, a single crystal was grown. The characteristics of the obtained single crystal is shown in the following Table 2.

15 Table 2

Crystal diameter	80mm	
Length of $\phi 80\text{mm}$ portion	100mm	
Carbon concentration	Shoulder	$1.4 \times 10^{15} \text{cm}^{-3}$
	Tail	$0.8 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$2.9 \times 10^7 \Omega\text{cm}$
	Tail	$1.5 \times 10^7 \Omega\text{cm}$
Dislocation density	Shoulder	$900\text{cm}^{-2}$
	Tail	$1200\text{cm}^{-2}$

In the present specification, the "shoulder" and "tail" of a crystal corresponds to the relevant portions

shown in Fig. 5.

The role of solid arsenic (As) sealed under reduced pressure in the quartz ampoule in the present example is set forth in the following.

5        The dissociation pressure at the melting point of GaAs is approximately 1 atm. When GaAs is melted, the airtight vessel is filled with As vapor of approximately 1 atm at the temperature of the melting point. This As vapor is generated as a result of the GaAs melt being decomposed.

10      Therefore, the composition of the GaAs melt is shifted from the original composition of Ga:As=1:1 to Ga rich composition. By sealing solid arsenic in the quartz ampoule in addition to GaAs, the shift from the composition of Ga:As=1:1 caused by decomposition of the

15      GaAs melt can be suppressed.

#### Example 2

Fig. 3 is a diagram for describing another example of a method of preparing a group III-V compound semiconductor crystal of the present invention.

20      Referring to Fig. 3, GaAs polycrystalline raw material 2, carbon fiber 23 subjected to heat treatment under reduced pressure in advance, boron oxide 4, and a seed crystal 7 were placed in a pBN crucible 1. Seed crystal 7 was placed at the bottom portion of the crucible

25      1. In crucible 1, arrangement was provided so that carbon

fiber 23 and boron oxide 4 were brought into contact with each other and also boron oxide 4 and raw material 2 were brought into contact with each other when the raw material was melted.

5           Crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Quartz ampoule 5 was sealed under reduced pressure with a quartz cap 6.

Respective conditions of Example 2 are shown in the following Table 3.

10

Table 3

GaAs polycrystal (raw material)	10kg used
Carbon fiber	Average diameter 5-8 $\mu$ m, 40mg used, Heat treatment at 800°C for 3 hours at the pressure of 10 <sup>-7</sup> Torr
B <sub>2</sub> O <sub>3</sub>	Water concentration 70 wt ppm, 100g used
pBN crucible	Inner diameter 105mm, entire length 400mm
Solid arsenic	1.5g used

Quartz ampoule 5 was heated at the rate of approximately 120°C/hour by a heater 8 using a vertical furnace 50, as shown in Fig. 2.

15           During the process of heating, boron oxide 4 was softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a film 4a having a thickness of not more than 1mm between pBN crucible 1 and GaAs melt 2. The remainder of boron oxide 4 covered the upper surface of the GaAs melt. This 5 boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 5mm. The carbon fiber 23 was partially dispersed in boron oxide layer 4b on GaAs melt 2, and partially floated. Furthermore, a portion of carbon fiber 23 was present also at the proximity of the 10 interface between GaAs melt 2 and boron oxide layer 4b.

Then, the condition mentioned above was kept for approximately 12 hours.

Then, heater 8 was moved upwards at the rate of 3mm/hour, whereby solidification started from the portion 15 of seed crystal 7. Thus, a single crystal was grown. The characteristics of the obtained single crystal are shown in the following Table 4.

---

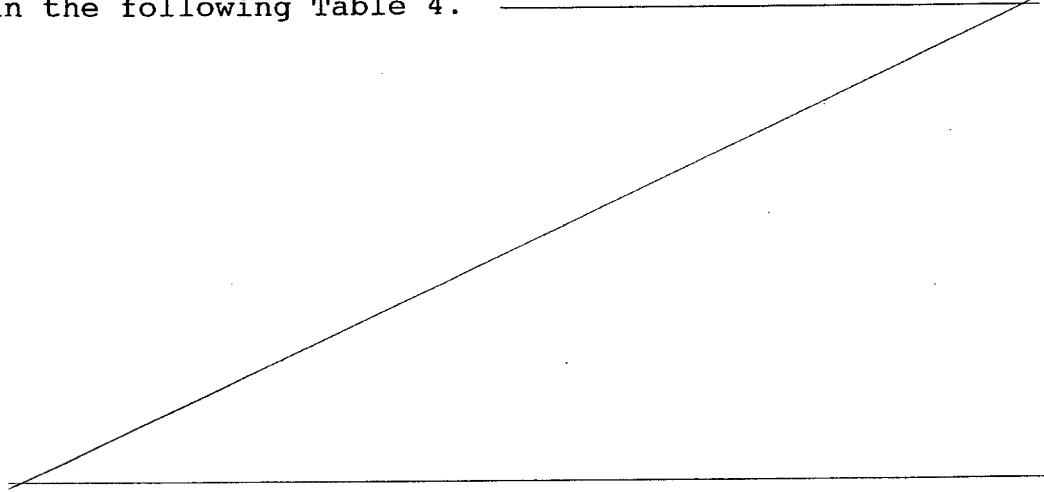


Table 4

Crystal diameter	105mm	
Length of $\phi 105\text{mm}$ portion	200mm	
Carbon concentration	Shoulder	$6.5 \times 10^{15} \text{cm}^{-3}$
	Tail	$7.0 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$4.1 \times 10^8 \Omega\text{cm}$
	Tail	$5.0 \times 10^8 \Omega\text{cm}$
Dislocation density	Shoulder	$800 \text{cm}^{-2}$
	Tail	$1500 \text{cm}^{-2}$

## Example 3

5 A carbon-doped GaAs single crystal was grown using 20 mg of carbon fiber similar to that of Example 2.

The other conditions of the experiment are identical to those of Example 2, and their description will not be repeated.

10 The characteristics of the obtained single crystal are shown in the following Table 5.

Table 5

Crystal diameter	105mm	
Length of $\phi 105\text{mm}$ portion	200mm	
Carbon concentration	Shoulder	$2.3 \times 10^{15} \text{cm}^{-3}$
	Tail	$2.2 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$8.8 \times 10^7 \Omega\text{cm}$
	Tail	$8.4 \times 10^7 \Omega\text{cm}$
Dislocation density	Shoulder	$1000 \text{cm}^{-2}$
	Tail	$1800 \text{cm}^{-2}$

Example 4

A carbon-doped GaAs single crystal was grown using 7.5mg of carbon fiber similar to those of Examples 2 and 3.

The other conditions are identical to those of Examples 2 and 3, and their description will not be repeated.

The characteristics of the obtained single crystal are shown in the following Table 6.

10 Table 6

Crystal diameter	105mm	
Length of $\phi 105\text{mm}$ portion	200mm	
Carbon concentration	Shoulder	$1.3 \times 10^{15}\text{cm}^{-3}$
	Tail	$1.2 \times 10^{15}\text{cm}^{-3}$
Resistivity	Shoulder	$2.5 \times 10^7\Omega\text{cm}$
	Tail	$2.3 \times 10^7\Omega\text{cm}$
Dislocation density	Shoulder	$1500\text{cm}^{-2}$
	Tail	$2000\text{cm}^{-2}$

15 It is appreciated from Examples 2, 3 and 4 that the carbon concentration in the crystal can easily be adjusted by just adjusting the amount of solid carbon to be doped according to the present invention.

Example 5

Fig. 4 is a diagram for describing another example of a method of preparing a group III-V compound semiconductor

crystal according to the present invention.

Referring to Fig. 4, GaAs polycrystalline raw material 2, a disk 43 made of sintered carbon powder subjected in advance to a heat treatment under reduced pressure, boron oxide 4, and a seed crystal 7 were placed in a pBN crucible 1. Seed crystal 7 was placed at the bottom portion of the crucible 1. In crucible 1, arrangement was provided so that carbon disk 43 and boron oxide 4 were brought into contact with each other, and also boron oxide 4 and raw material 2 were brought into contact with each other when the raw material was melted.

This crucible 1 was inserted in a quartz ampoule 5 together with solid arsenic. Quartz ampoule 5 was sealed under reduced pressure using quartz cap 6.

Respective conditions of example 4 are indicated in the following Table 7.

Table 7

GaAs polycrystalline raw material	3kg used
Carbon disk	Diameter 30mm, thickness 10mm used Heat treatment at 1500°C for 12 hours at the pressure of 1 Torr
B <sub>2</sub> O <sub>3</sub>	Water concentration 300 wt ppm, 50g used
pBN crucible	Inner diameter 80mm, entire length 250mm
Solid arsenic	1g used

The above-described quartz ampoule 5 was heated at the rate of approximately 200°C/hour by heater 8 using 5 vertical furnace 50.

During the process of heating, boron oxide 4 was softened and melted. Also, GaAs polycrystalline raw material 2 was melted.

At this time point, boron oxide 4 was present as a 10 film 4a having a thickness of less than 1mm between pBN crucible 1 and GaAs melt 2. The remainder of boron oxide 4 covered the upper surface of GaAs melt 2. The thickness of the boron oxide layer 4b covering the upper surface of GaAs melt 2 was approximately 6mm. Carbon disk 43 had its 15 bottom surface in contact with raw material melt 2, and its top surface exposed to the ambient. The side surface thereof was surrounded by boron oxide layer 4b.

The condition mentioned above was kept for

approximately 6 hours.

Then, heater 8 was moved upwards at the rate of 4mm/hour, whereby solidification started from the portion of seed crystal 7. Thus, a single crystal was grown. The 5 characteristics of the obtained single crystal are shown in the following Table 8.

Table 8

Crystal diameter	80mm	
Length of $\phi 80$ mm portion	100mm	
Carbon concentration	Shoulder	$6.8 \times 10^{15} \text{cm}^{-3}$
	Tail	$7.1 \times 10^{15} \text{cm}^{-3}$
Resistivity	Shoulder	$4.5 \times 10^8 \Omega\text{cm}$
	Tail	$5.2 \times 10^8 \Omega\text{cm}$
Dislocation density	Shoulder	$1200 \text{cm}^{-2}$
	Tail	$1500 \text{cm}^{-2}$

10 In a semi-insulating GaAs crystal, the resistivity is one of the most important characteristics. It is preferable that variation in resistivity is smaller. Furthermore, since this resistivity value depends on the carbon concentration in the GaAs crystal, variation in the 15 carbon concentration in the crystal should be as small as possible.

In the above-described examples where carbon fiber or bulk carbon was used as the solid carbon, the carbon was

doped substantially uniformly from the shoulder to the tail of the crystal. It is appreciated that carbon fiber and bulk carbon are preferable as solid carbon sources. The shape of bulk carbon is not limited to the disk shape shown in Example 5, and any shape can be used. Also, bulk carbon is preferably a sintered compact of carbon powder.

Comparison of the effect of the present invention depending upon difference in the type of solid carbon is shown in the following Table 9.

10

Table 9

Difference in effect among powder, fiber, and bulk carbon

Type of solid carbon	Carbon distribution in a crystal from shoulder to tail
Carbon powder	Gradual decrease of carbon from shoulder to tail
Carbon fiber	Uniform distribution of carbon from shoulder to tail
Bulk carbon	Uniform distribution of carbon from shoulder to tail

Comparison of the carbon concentration in a GaAs crystal between the present invention and the prior art is shown in the following Table 10.

Table 10

Comparison of carbon concentration in GaAs crystal

		Carbon concentration (cm <sup>-3</sup> )	
		Shoulder	Tail
Present invention	Carbon powder	$1.4 \times 10^{15}$	$0.8 \times 10^{15}$
	Carbon fiber	Example 2	$6.5 \times 10^{15}$
		Example 3	$2.3 \times 10^{15}$
		Example 4	$1.3 \times 10^{15}$
	Carbon disk	$6.8 \times 10^{15}$	$7.1 \times 10^{15}$
Prior art	Prior art 2	$0.5 \times 10^{15}$	$0.4 \times 10^{15}$
	Prior art 3	$2.2 \times 10^{15}$	$1.4 \times 10^{15}$

Although the present invention has been described and  
 5 illustrated in detail, it is clearly understood that the  
 same is by way of illustration and example only and is not  
 to be taken by way of limitation, the spirit and scope of  
 the present invention being limited only by the terms of  
 the appended claims.

WHAT IS CLAIMED IS:

1. A method of preparing a group III-V compound semiconductor crystal having carbon doped, comprising the steps of:

filling a crucible or a boat with compound raw  
5 material, solid carbon, and boron oxide,  
sealing said crucible or boat filled with said  
compound raw material, said solid carbon, and said boron  
oxide within an airtight vessel formed of a gas  
impermeable material,  
10 heating and melting said compound material in the  
sealed state within said airtight vessel, and  
solidifying said melted compound material to grow a  
carbon-doped compound semiconductor crystal.

2. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said step of heating and melting the compound material comprises the step of heating and melting said boron oxide  
5 to bring the heat-melted boron oxide into contact with at least a portion of the solid carbon.

3. The method of preparing a group III-V compound

semiconductor crystal according to claim 1, wherein said gas impermeable material comprises a material selected from the group consisting of quartz and pBN.

4. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said boron oxide contains water.

5. The method of preparing a group III-V compound semiconductor crystal according to claim 4, wherein said boron oxide contains water of 10-500 wt ppm.

6. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein an amount of said filled solid carbon is larger than the amount of carbon doped into said compound semiconductor crystal.

7. A method of preparing a group III-V compound semiconductor crystal according to claim 6, wherein the amount of said filled solid carbon is at least 10 times larger than the amount of carbon doped into said compound semiconductor crystal.

8. The method of preparing a group III-V compound

semiconductor crystal according to claim 1, wherein said solid carbon is subjected to a heat treatment under reduced pressure before filling said crucible or boat.

9. The method of preparing a group III-V compound semiconductor crystal according to claim 8, wherein said heat treatment is carried out for 1 hour to 12 hours at a temperature of 500°C-2000°C under a pressure of 1 Torr - 1  
5  $\times 10^{-8}$  Torr.

10. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said melted compound raw material is kept in a melted state for a certain time period before being solidified to grow a  
5 crystal.

11. The method of preparing a group III-V compound semiconductor crystal according to claim 10, wherein said melted compound raw material is kept in a melted state for 3-72 hours.

12. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said solid carbon comprises powder carbon.

13. The method of preparing a group III-V compound semiconductor crystal according to claim 12, wherein said powder solid carbon has a grain size of not more than 100 $\mu$ m.

14. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said solid carbon comprises fiber carbon.

15. The method of preparing a group III-V compound semiconductor crystal according to claim 14, wherein said fiber solid carbon has an average diameter of not more than 50 $\mu$ m.

16. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said solid carbon comprises bulk carbon.

17. The method of preparing a group III-V compound semiconductor crystal according to claim 16, wherein said bulk solid carbon has a disk shape smaller than an inner diameter of said crucible.

18. The method of preparing a group III-V compound semiconductor crystal according to claim 16, wherein said

bulk solid carbon comprises a sintered compact of carbon powder.

19. A method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said crucible or boat comprises pBN.

20. The method of preparing a group III-V compound semiconductor crystal according to claim 1, wherein said group III-V compound semiconductor crystal comprises a GaAs crystal.

## ABSTRACT OF THE DISCLOSURE

A method of preparing in high reproducibility a group III-V compound semiconductor crystal of favorable electrical characteristics with impurities removed, and in which the 5 amount of doped carbon can be adjusted easily in crystal growth is provided. This method of preparing a carbon-doped group III-V compound semiconductor crystal includes the steps of: filling a crucible with compound raw material, solid carbon, and boron oxide; sealing the 10 crucible filled with compound material, solid carbon, and boron oxide within an airtight vessel formed of a gas impermeable material; heating and melting the compound material under the sealed state in the airtight vessel; and solidifying the melted compound material to grow a 15 carbon-doped compound semiconductor crystal.

# Declaration and Power of Attorney For Patent Application

## 特許出願宣言書

### Japanese Language Declaration

私は、下欄に氏名を記載した発明者として、以下のとおり宣言する：

私の住所、郵便の宛先および国籍は、下欄に氏名に続けて記載したとおりであり、

名称の発明に関し、請求の範囲に記載した特許を求める主題の本来の、最初にして唯一の発明者である（一人の氏名のみが下欄に記載されている場合）か、もしくは本来の、最初にして共同の発明者である（複数の氏名が下欄に記載されている場合）と信じ、

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

その明細書を  
(該当する方に印を付す)

ここに添付する。

\_\_\_\_\_ 日に出願番号

第 \_\_\_\_\_ 号として提出し、

\_\_\_\_\_ 日に補正した。  
(該当する場合)

Method of Preparing Group III-V

Compound Semiconductor Crystal

the specification of which

(check one)

is attached hereto.

was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and was amended on \_\_\_\_\_ (if applicable)

私は、前記のとおり補正した請求の範囲を含む前記明細書の内容を検討し、理解したことを陳述する。

私は、連邦規則法典第37部第1章第56条 項に従い、本願の審査に所要の情報を開示すべき義務を有することを認める。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

## Japanese Language Declaration

私は、合衆国法典第35部第119条にもとづく下記の外国特許出願または発明者証出願の外国優先権利益を主張し、さらに優先権の主張に係わる基礎出願の出願日前の出願日を有する外国特許出願または発明者証出願を以下に明記する：

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

### Prior foreign applications

### 先の外国出願

## Priority claimed 優先権の主張

8-107009 Pat.	Japan (Country) (国名)	26/April/1996 (Day/Month/Year Filed) (出願の年月日)	<input checked="" type="checkbox"/> Yes あり	<input type="checkbox"/> No なし
(Number) (番号)				
(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)	<input type="checkbox"/> Yes あり	<input type="checkbox"/> No なし
(番号)				
(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願の年月日)	<input type="checkbox"/> Yes あり	<input type="checkbox"/> No なし
(番号)				

私は、合衆国法典第35部第120条にもとづく下記の合衆国特許出願の利益を主張し、本願の請求の範囲各項に記載の主題が合衆国法典第35部第112条第1項に規定の態様で先の合衆国出願に開示されていない限度において、先の出願の出願日と本願の国内出願日またはPCT国際出願日の間に公表された連邦規則法典第37部第1章第56条項に記載の所要の情報を開示すべき義務を有することを認め  
る：

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (出願番号)	(Filing Date) (出願日)	(現況) (特許済み、係属中、放棄済み)	(Status) (patented, pending, abandoned)
(Application Serial No.) (出願番号)	(Filing Date) (出願日)	(現況) (特許済み、係属中、放棄済み)	(Status) (patented, pending, abandoned)

私は、ここに自己の知識にもとづいて行った陳述がすべて真実であり、自己の有する情報および信ずるところに従って行った陳述が真実であると信じ、さらに故意に虚偽の陳述等を行った場合、合衆国法典第18部第1001条により、罰金もしくは禁錮に処せられるか、またはこれらの刑が併科され、またかかる故意による虚偽の陳述が本願ないし本願に対して付与される特許の有効性を損うことがあることを認識して、以上の陳述を行ったことを宣言する。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## Japanese Language Declaration

委任状：私は、下記発明者として、以下の代理人をここに選任し、本願の手続を遂行すること並びにこれに関する一切の行為を特許商標庁に対して行うことを委任する。  
(代理人氏名および登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (list name and registration number)

W. G. Fasse - Reg. No.: 21187

W. F. Fasse - Reg. No.: 36132

書類の送付先：

Send Correspondence to: W. G. Fasse  
Indian Pond Lane, P. O. Box K  
St. Albans, Maine 04971  
U. S. A.

直通電話連絡先：(名称および電話番号)

Direct Telephone Calls to: (name and telephone number)  
W. G. Fasse - (207) 938-4422

唯一のまたは第一の発明者の氏名	Full name of sole or first inventor Tomohiro KAWASE	
同発明者の署名	日付	Date <i>Tomohiro Kawase</i> April 21, 1997
住所	Residence Hyogo, Japan	
国籍	Citizenship Japanese	
郵便の宛先	Post Office Address c/o Itami Works of Sumitomo Electric Industries, Ltd., 1-1, Koyakita 1-chome, Itami-shi, Hyogo, Japan	
第2の共同発明者の氏名 (該当する場合)	Full name of second joint inventor, if any Masami TATSUMI	
同第2発明者の署名	日付	Date <i>Masami Tatsumi</i> April 21, 1997
住所	Residence Hyogo, Japan	
国籍	Citizenship Japanese	
郵便の宛先	Post Office Address c/o Itami Works of Sumitomo Electric Industries, Ltd., 1-1, Koyakita 1-chome, Itami-shi, Hyogo, Japan	

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)